

19. Hybrid discrete dislocation models for fatigue crack growth / Curtin W. A., Deshpande V. S., Needleman A., Van der Giessen E., Wallin M. // International Journal of Fatigue. 2010. Vol. 32, Issue 9. P. 1511–1520. doi: 10.1016/j.ijfatigue.2009.10.015
20. Effect of load amplitude change on the fatigue life of cracked Al plate repaired with composite patch / Albedah A., Khan S. M. A., Benyahia F., Bachir Bouiadja B. // International Journal of Fatigue. 2016. Vol. 88. P. 1–9. doi: 10.1016/j.ijfatigue.2016.03.002
21. Broek D. Elementary Engineering Fracture Mechanic. 4th ed. Springer, 1982. 540 p.
22. Kern M., Berger P., Hügel H. Magneto-Fluid Dynamics Control Of Seam Quality In CO2 Laser Beam Welding // Welding Research Supplement. 2000. P. 72s–78s.
23. Tse H. C., Man H. C., Yue T. M. Effect of electric and magnetic fields on plasma control during CO2 laser welding // Optics and Lasers in Engineering. 1999. Vol. 32, Issue 1. P. 55–63. doi: 10.1016/s0143-8166(99)00045-7
24. Dar Y. A., Singh C., Farooq Y. Effects of External Magnetic Field on Welding Arc of Shielded Metal Arc Welding // Indian Journal of Applied Research. 2011. Vol. 4, Issue 4. P. 200–203. doi: 10.15373/2249555x/apr2014/60
25. Senapati A., Mohanty S. brata. Effects of External Magnetic Field on Mechanical properties of a welded M.S metal through Metal Shield Arc Welding // International Journal of Engineering Trends and Technology. 2014. Vol. 10, Issue 6. P. 297–303. doi: 10.14445/22315381/ijett-v10p258
26. Metallurgical Characterization of API X65 Steel Joint Welded by MIG Welding Process with Axial Magnetic Field / Natividad C., García R., López V. H., Contreras A., Salazar M. // Materials Research. 2017. Vol. 20, Issue 5. P. 1174–1178. doi: 10.1590/1980-5373-mr-2016-0182

Досліджено вплив робочих параметрів плазмово-електролітичного оксидування у дифосфатному кобальтмісному електроліті на процес формування оксидних покриттів на сплаві АЛ25. Встановлено, що склад та морфологія поверхні одержаних шарів $Al_2O_3 \cdot CoO_x$ залежать від густини струму обробки та часу оксидування. Варіювання параметрів ПЕО дозволяє гнучко керувати процесом інкорпорації каталітичного компонента в матрицю оксиду основного металу. Обґрунтовано раціональний режим обробки поршневого силуміну для формування збагачених кобальтом оксидних покриттів

Ключові слова: поршковий силумін, АЛ25, плазмово-електролітичне оксидування, оксидний покриття, морфологія поверхні

Исследовано влияние рабочих параметров плазменно-электролитического оксидирования в дифосфатном кобальтсодержащем электролите на процесс формирования оксидных покрытий на сплаве АЛ25. Установлено, что состав и морфология поверхности сформированных оксидных слоев $Al_2O_3 \cdot CoO_x$ зависят от плотности тока обработки и времени оксидирования. Варьирование параметров ПЭО позволяет гибко управлять процессом инкорпорации каталитического компонента в матрицу оксида основного металла. Обоснован рациональный режим обработки поршневого силумина для получения обогащенных кобальтом оксидных покрытий

Ключевые слова: поршневой силумин, АЛ25, плазменно-электролитическое оксидирование, оксидное покрытие, морфология поверхности

UDC 621.35

DOI: 10.15587/1729-4061.2018.128457

STUDY OF THE INFLUENCE OF OXIDIZING PARAMETERS ON THE COMPOSITION AND MORPHOLOGY OF $Al_2O_3 \cdot CoO_x$ COATINGS ON AL25 ALLOY

A. Karakurkchi

PhD, Senior Researcher*

E-mail: anyutikukr@gmail.com

M. Sakhnenko

Doctor of Technical Sciences,

Professor, Head of Department**

E-mail: sakhnenko@kpi.kharkov.ua

M. Ved

Doctor of Technical Sciences, Professor*

E-mail: vmv@kpi.kharkov.ua

Department of Physical Chemistry*

*Department of General and Inorganic Chemistry***

***National Technical University

«Kharkiv Polytechnic Institute»

Kyrpychova str., 2, Kharkiv, Ukraine, 61002

1. Introduction

Alloying of silumins with additional components allows great expansion of the scope of their application. Al-Si alloys are successfully applied in various industries, specifically for

manufacturing parts of a cylinder-piston group of internal combustion engines (ICE) [1, 2].

Additional techniques of surface modification are effectively used for improvement of mechanical properties of silumins. One of the approaches involves electrochemical

treatment using the method of plasma electrolytic oxidation (PEO) in alkaline electrolytes to form firmly adhesive oxide coatings of different thickness on the surface of the material [3, 4].

The peculiarities of electrochemical and thermo-chemical reactions realization during the treatment and varying the electrolyte composition make it possible to obtain a highly developed surface of alumina matrix, doped by electrolyte components [5].

Among the advantages of PEO-treatment, it is necessary to note the non-toxicity of working solutions, simplicity of the used equipment and possibility of oxidizing of products with a complex geometry.

The obtained oxide coatings give a surface high mechanical [6], protective [7], catalytic [8] properties due to the introduction of transition and refractory components to the composition of surface layers.

At the same time, a PEO of Al-Si alloy is a rather complicated technological process. Surface heterogeneity of such materials and, as a consequence, different conductivity of oxides of alloy components requires correction of the used electrolyte composition and technological oxidation process [9].

The study of processes of the surface plasma-electrolytic treatment of silumins with formation of oxide coatings is a relevant practical problem. Its solution will make it possible to expand the scope of application of aluminosilicon alloys due to enhancement of their performance.

2. Literature review and problem statement

PEO is widely used for modification of the surface of silumins with different content of silicon. At the same time, a large number of alloying components inter-metallic compounds and silicon in the alloy composition significantly affect the process of its electrochemical treatment. Oxidation conditions, the type of the working electrolyte and the nature of doping components predetermine the features of the technological process of treatment and properties of the formed oxide coatings.

The author of paper [10] studied the process of PEO-treatment of silumins with silicon content from 6 up to 21.5 % in alkaline pyrophosphate electrolytes. It was shown that inhibition of the oxide layer growth by silicon particles in the oxidizing process is observed. This leads to a decrease in thickness of the formed oxide coating, an increase in its porosity and a decrease in adhesion with the treated alloy. It was established that directed surface modification of silumins is possible due to a change in oxidation time and thermal pre-treatment of alloys to reduce the content of silicon in the surface layer.

Based on the results of research, authors of papers [11, 12] also found that silicon particles in the alloy composition and Si-containing phases inhibit aluminum oxidation and affect morphology and composition of obtained coatings. Therefore, to obtain uniformed oxide layers, it is appropriate to conduct silumin oxidation in the micro-arc mode at treatment time of not less than 60 minutes.

Al-Si alloys oxidation in alkali silicate electrolytes is most common. It is proved by the significant number of studies on formation of PEO-coatings on piston alloys in electrolytes of this type.

Authors of article [13] showed that when treated in alkaline silica electrolyte, the surface of the coating was formed

by craters of aluminum oxide with inclusion of knotty silicon structures, which is explained by its high content in the structure of the alloy. A clear correlation between the PEO stages, the time of samples treatment and the microstructure of obtained coatings was shown. The authors made a conclusion about the necessity of forming coatings in the micro-arc mode in order to obtain the uniformed oxide layer.

In papers [14, 15], oxide coatings on AK12D alloy were formed by PEO-treatment in alkali silicate electrolytes in the anode-cathode mode at current density of 2.5 12 A/dm². The cross-sections of the obtained coatings were studied. It was shown that the formed oxide layers consist mostly of aluminum oxide and demonstrate improved thermal and mechanical properties. Silicon content varies from 1 to 18 at. %. Other alloying components of the alloy in the composition of coatings were not detected.

Authors of [16] obtained the oxide coating consisting mostly of aluminum and silicon oxides by silumin oxidation in the silicate electrolyte at current density of 20 A/dm². It was noted that morphology of the surface layer depends on duration of sample treatment. When oxidation time increases, porosity of coatings decreases and the degree of surface development increases due to the growth of surface remelts of the basic metal and electrolyte components.

In paper [17], PEO-treatment of silumin was conducted in the complex silicate electrolyte at fixed current density of 10 A/dm². Oxidizing time was changed from 1 up to 15 min. The authors found that there are sections of different morphology on the surface of the formed oxide layer, which is explained by the structural characteristics of aluminum alloy. At the same time, morphology of the surface layer and chemical composition of the coating change at an increase in oxidation time.

Thus, the above analysis of experimental studies indicates the possibility of PEO-treatment of silumins in silicate electrolytes. In this case, existence of silicon in the composition of working solutions leads to the fact that its content in the formed oxide layers of high enough. By the results of the research into the properties of these systems [15, 18], it was found that such coatings have enhanced thermo-mechanical characteristics.

With a view to effective silicon removal from the surface layer and giving the treated surface a wider spectrum of functional characteristics, it is appropriate to use complex electrolytes with addition salts of metal-dopants. The obtained metal-oxide systems can be used effectively in environmental catalysis [19]. Transition metals are optimal dopants for using in catalytic reactions.

Authors of paper [20] present results of obtaining coatings, doped by manganese and zinc in the diphosphate electrolyte. The treatment is carried out within 10 minutes in the galvanostatic mode, current density of oxidation is 0.05 A/cm². The results of the phase analysis proved incorporation of oxidized forms of metals in the formed oxide layer. Impurity content in coatings is negligible.

The author of the article [21] gives results of the studies on obtaining oxide coatings, doped with manganese. Treatment of aluminum alloy AMcM was carried out in polyphosphate electrolyte at current density of 5 A/dm², duration of treatment ranged from 1.5 to 16 minutes. In these circumstances, coatings with the content of a dopant up to 20 % by weight were obtained. Enrichment of the surface layer with manganese is observed at an increase in time of PEO-treatment.

In article [22], alkaline permanganate electrolyte was used for PEO of AL25 alloy, silumin was treated in the step-wise mode at varying current density within 5–25 A/dm². Sparking voltage for the studied solutions was 80–150 V, final formation voltage was 180–240 V. As a result of research, it was found that treatment at a higher current density is more preferable. This allows obtaining oxide coatings of more thickness with manganese content of up to 36 at. %. At the same time, the content of Si in the surface oxide layer varies widely from 0.4 up to 13.4 at. %.

In article [23], PEO of aluminum alloy was conducted in complex electrolytes based on sodium tetraborate with the addition of Trilon B. Oxidation was carried out in the anodic-cathodic mode at current density of 100 mA/cm². Maximum formation voltage was 350 V. It was found that obtained oxide coatings contain cobalt up to 4.13 at. %, and are characterized by significant porosity. Si content in the surface layer reaches 10 at. %. The author made conclusion about a quite uniform distribution of a dopant on the surface of the obtained coating.

In paper [24], authors presented the results of obtaining cobalt-containing coatings on valve metals in borate-phosphate electrolyte with addition of cobalt acetate. It was shown that it is possible to obtain oxide coatings, enriched with cobalt, by oxidation within 20 minutes at current density of 0.08 A/cm².

Authors of papers [25, 26] conducted PEO-treatment in silicon-acetate electrolyte at current density of 10 and 20 A/dm², oxidation time was 10 min. It was shown that higher formation voltage, and as a result, higher cobalt content is observed at PEO current density $i=20$ A/dm². Morphology of the surface is heterogeneous with lots of projections of irregular shape. Cobalt content in coatings does not exceed 10 at. %.

Obtained results suggest quite a complex mechanism of reactions in working solutions during oxidizing of valve metals. Complexity of silumins composition and large amount of silicon in the surface layers complicate the processes of dopant incorporation in the formed oxide coating. It is preferable to use complex electrolytes based on diphosphates.

Electrolyte composition, voltage indicators, current density and oxidation time are important technological parameters for the PEO process [5]. By changing these characteristics, it is possible to make flexible control of the process of the surface electrochemical treatment and formation of an oxide layer. In doing so, the authors did not sufficiently show the data on characteristics of the process. Working current densities and treatment time are usually chosen empirically. This complicates verification of the obtained data.

3. The aim and objectives of the study

The aim of present study is to examine the influence of current density and oxidation time on the composition and morphology of cobalt-containing oxide coatings on AL25 alloy obtained in diphosphate electrolyte. This will allow selecting optimum parameters of the process of piston alloy treatment to form functional materials with varied content of a catalytic active component.

To accomplish the aim, the following tasks have been set:
– to explore the change in oxidation voltage and the time of entering the sparking mode at PEO of AL25 alloy (GOST 1583) in diphosphate cobalt containing electrolyte at varying current density;

– to examine dependence of surface morphology and composition of oxide coatings on current density and formation time;

– to substantiate the mode of obtaining oxide PEO-coatings with high cobalt content and specified surface morphology.

4. Procedure for obtaining Al₂O₃-CoO_x coatings; study of their composition and morphology

4. 1. Method of obtaining

Cobalt-containing oxide coatings were formed on the samples from piston silumin AL25. Chemical composition of AL25 alloy is given in Table 1.

Table 1

Chemical composition of AL25 alloy (GOST 1583), %

Al	Si	Mn	Mg	Ni	Fe	Cr	Ti	Cu	Pb	Zn	Sn	Impurities
79.5–85.55	11–13	0.3–0.6	0.8–1.3	0.8–1.3	up to 0.8	up to 0.2	0.05–0.2	1.5–3.0	up to 0.1	up to 0.5	up to 0.02	total 1.3

Electrolyte of the following composition, mol/dm³: 0.4 K₄P₂O₇, 0.1 CoSO₄; pH 9.5 was used for PEO. Certified reagents of chemically pure grade and distilled water were used for the preparation of working solutions.

PEO was conducted in the galvanostatic mode. The laboratory setup was used to form coatings. It included the industrial stabilized power source B5-50 (Ukraine), an electrolytic cell with forced cooling and stirring, an ammeter and a voltmeter. The temperature of the electrolyte was maintained within 20–25 °C.

Oxidation current density varied in the range of 1–10 A/dm². The time of coatings formation was 2–60 minutes. PEO stages were controlled visually and recorded according to the readings of the devices.

The surface of samples for coatings application was prepared by grinding with subsequent degreasing, washed with water, and dried at a temperature of 30 °C.

4. 2. Methods for studying Al₂O₃-CoO_x coatings

Morphology of the formed oxide coatings surface was studied using the scanning electron microscope ZEISS EVO 40XVP (Germany). Topography of the coatings surface was studied through the atomic-power microscope NT-206 using the probe CSC-37. Chemical composition of the oxide coatings was determined on energy-dispersion spectrometer Oxford INCA Energy 350 (Great Britain) with the integrated program environment SmartSEM.

5. Results of formation of Al₂O₃-CoO_x coatings on AL25 alloy

Surface modification of valve metals can be efficiently carried out using diphosphates-based electrolytes [27, 28].

As noted in the study [9], chronograms of formation voltage of oxide coatings on highly silicon alloy in cobalt-con-

taining diphosphate electrolytes of different concentrations have a classic form. This was also proved for the process of obtaining $\text{Al}_2\text{O}_3\cdot\text{CoO}_x$ coatings on AL25 alloy at different current densities (Fig. 1).

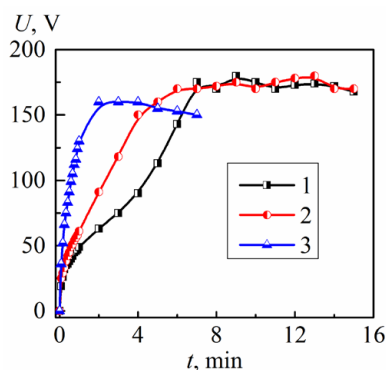


Fig. 1. Chronograms of formation voltage at oxidation of AL25 alloy in diphosphate electrolytes at different current densities, A/dm^2 : 1 – 3; 2 – 5; 3 – 10

In the pre-spark area, the process is characterized by formation of a barrier layer of aluminum oxide. That is why the sections of dependences $U-t$ are linear in character. Angle of slope of formation chronogram in the initial section reflects oxidation rate, which increases at an increase in current density from 3 to 10 A/dm^2 . It should be noted that chronograms at $i=3-5 \text{ A}/\text{dm}^2$ are characterized by existence of a kink in the pre-sparking area in the time interval of 1–2 min, and in this case, a kink is more pronounced at lower current density (Fig. 1, dependence 1).

Time of entering the sparking mode decreases from 6 to 1 min at an increase in current density i at the studied interval. Sparking voltage in all cases is 120–125 V. Sparking intensity in the oxidation process is quite high.

The final formation voltage depends on initial current density of PEO. For $i=3-5 \text{ A}/\text{dm}^2$ U_i is 160–170 V and enables conducting the process of PEO-treatment within 15 min or longer. At the initial current density of 10 A/dm^2 , this indicator does not exceed 160 V. The oxidation process rapidly goes through all stages and from the 4th minute enters the arc mode. In this case, PEO of the alloy after 8 min is impractical; the formed coating is destroyed under the influence of arc discharges.

The influence of current density is sufficiently evident in the change of surface morphology of resulting oxide coatings (Fig. 2).

In the PEO process, cobalt incorporation into the composition of oxide layers occurs in the form of drop-shaped and spherical inclusions of blue-purple color. With an increase in oxidation current density from 3 to 5 A/dm^2 , their number increases, they form mosaic structures and evenly cover the entire surface of the sample. The resulting ceramic-like coating has high adhesion to the substrate. Oxidation of samples at i of 10 A/dm^2 leads to cobalt incorporation in the form of voluminous islet structures. Given a quite rapid transition of PEO into the arc mode, there is a tendency to these inclusions peeling off from the basis.

As a result of PEO of piston silumin, aluminum oxide matrix with incorporated remelts of the components of electrolyte and the alloy itself is formed (Fig. 3).

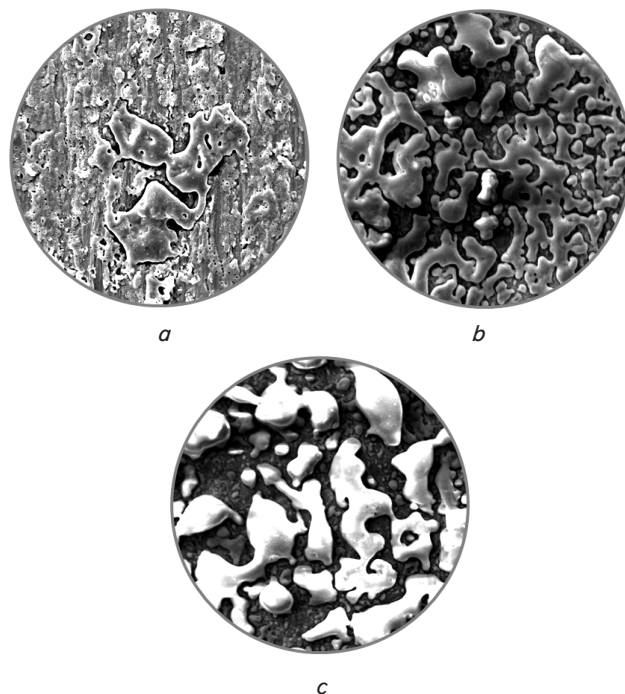


Fig. 2. Surface morphology of $\text{Al}_2\text{O}_3\cdot\text{CoO}_x$ coatings, obtained at different current densities, A/dm^2 : *a* – 3; *b* – 5; *c* – 10. Magnification $\times 500$

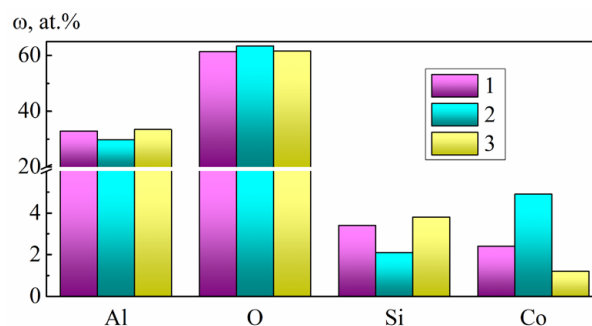


Fig. 3. Composition of $\text{Al}_2\text{O}_3\cdot\text{CoO}_x$ coatings (Fig. 2), formed at different current densities, A/dm^2 : 1 – 3; 2 – 5; 3 – 10

An increase in oxidizing current density was found to contribute to a decrease in silicon content in the surface layers of formed oxide coatings by 3–5 times compared to the treated alloy [29]. $\omega(\text{Si})$ does not exceed 4 at. % for the treated samples. In this case, the content of aluminum and oxygen in coatings at varying of i changes in the range of only 2–3 at. %.

Content of catalytically active component is an important characteristic for catalytic properties of PEO-based systems [30]. The coating with the highest cobalt content was obtained at current density of 5 A/dm^2 . It also contains the least amount of silicon – 2.1 at. %. Minimal inclusion of cobalt is ensured in the oxidation process at $i=10 \text{ A}/\text{dm}^2$. Variation in time of treatment of piston silumin AL25 also makes it possible to obtain oxide coatings of different morphology (Fig. 4).

The surface of coatings changes from unevenly rough (Fig. 4, *a*) to uniform mosaic (Fig. 4, *b*) and further to globular-mosaic (Fig. 4, *c*) at an increase in oxidation time from 10 to 40 min. Oxidation within 60 min or more leads to “overgrowing” of the voluminous structure and its visual alignment (Fig. 4, *d*).

Surface of obtained $\text{Al}_2\text{O}_3\cdot\text{CoO}_x$ coatings (Fig. 4) is characterized by existence of areas of different topography. For SAM, the shown area 1 is positioned as a projection of the coating (globule for a voluminous structure). Area 2 is determined as a plateau and corresponds to the matrix of aluminum oxide. These areas (Fig. 4, *a–d*) are selected for comparative analysis of the formed oxide coatings.

The results of the study (Fig. 5) indicate that in all cases projections (globules) of the coatings are enriched with cobalt and contain less silicon than the plateau. Depending on treatment time, Co content varies in the range of 0.1 to

23.3 at. %, Si content varies from 1.7 to 11.6 at. %. Aluminum concentration on the plateau is higher than on the globules. Oxygen content in the surface layer in all areas of coatings reflects the fact of formation of non-stoichiometric cobalt oxides.

The study of morphology and chemical composition of the surface layers makes it possible to conclude that PEO-treatment of AL25 alloy in diphosphate electrolyte with addition of cobalt sulfate leads to formation of a sufficiently developed voluminous structure. This statement is proved by the results of studies of surface topography of the formed oxide layers by the contact method (Fig. 6).

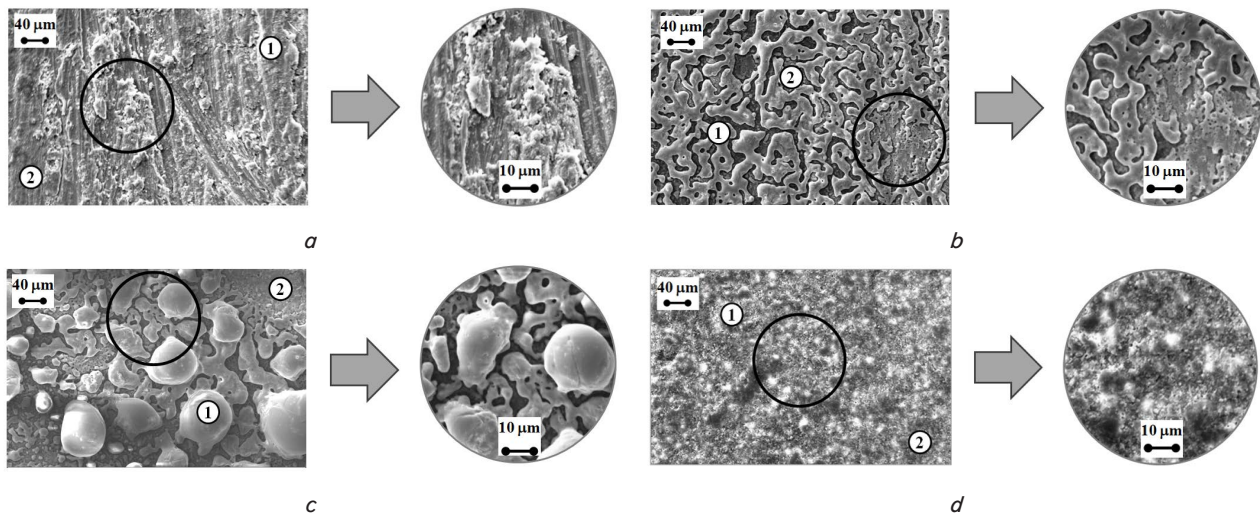


Fig. 4. Morphology of surface of $\text{Al}_2\text{O}_3\cdot\text{CoO}_x$ coating on AL25, obtained in diphosphate electrolyte at different oxidation time, min: *a* – 10; *b* – 20; *c* – 40; *d* – 60. Magnification $\times 500$ and $1,000$

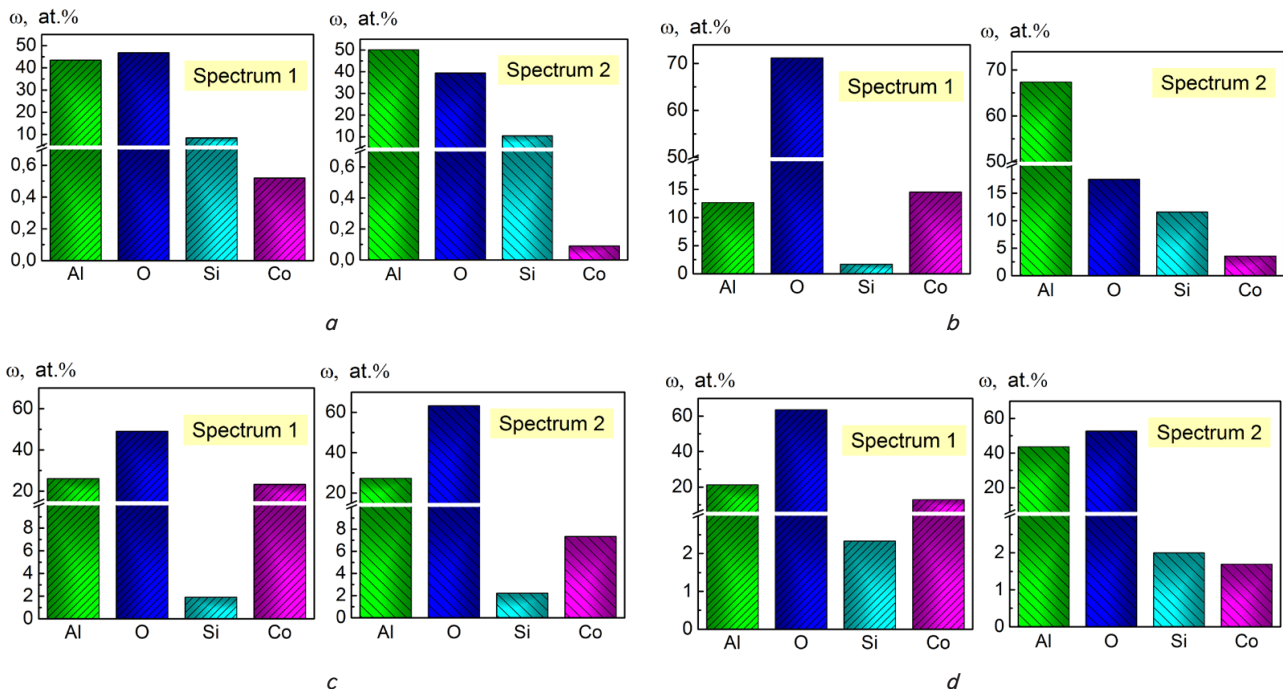


Fig. 5. Chemical composition of areas 1 and 2 (Fig. 4) of $\text{Al}_2\text{O}_3\cdot\text{CoO}_x$ coatings on AL25 at different oxidation time, min: *a* – 10; *b* – 20; *c* – 40; *d* – 60

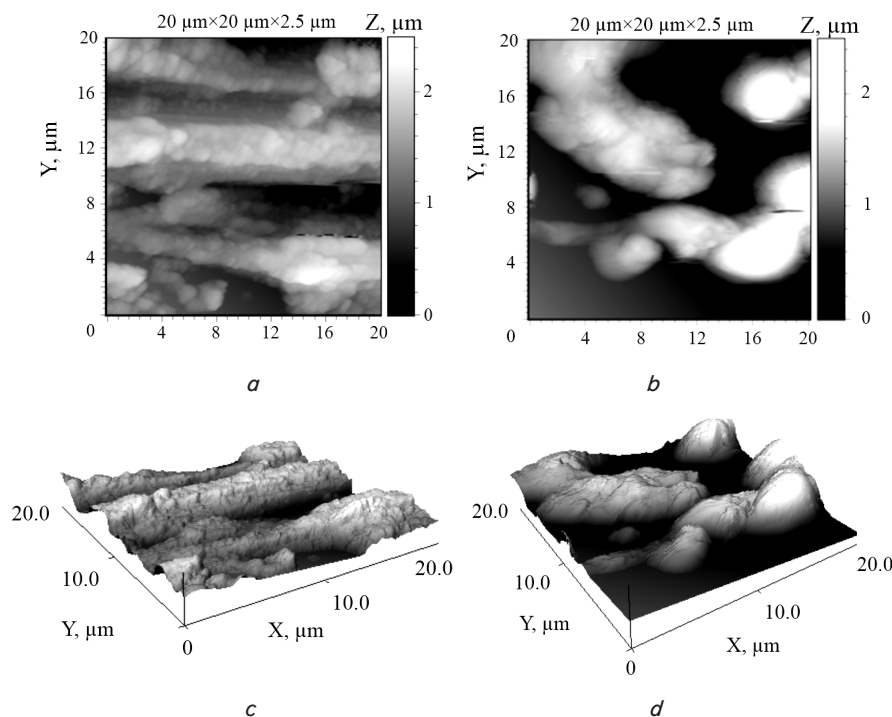


Fig. 6. Topography of the surface of $\text{Al}_2\text{O}_3\text{-CoO}_x$ coating on AL25, formed at current density of 5 A/dm² within, min: *a*, *c* – 10, *b*, *d* – 20, *a*, *b* – 2D-map, *c*, *d* – 3D-map. Scan area 20×20 μm

The obtained results of the impact of current density and oxidation time make it possible to determine the ways of controlling composition and morphology of the surface of oxide layers at PEO-treatment of piston alloy AL25 in cobalt-containing diphosphate electrolyte.

6. Discussion of the influence of oxidation parameters on composition and morphology of $\text{Al}_2\text{O}_3\text{-CoO}_x$ coatings on AL25

Chemical composition of piston silumin AL25 is characterized by a large number of alloying components and non-homogeneity of their distribution on the surface. Therefore, it is advisable to use alkaline diphosphate electrolyte with addition of salt of the metal-dopant for the surface treatment.

Homogenization of the surface of the treated alloy and formation of uniform oxide coatings, doped with additional components is achieved by selection of optimal PEO mode and oxidation time [9].

The oxidation of AL25 alloy at current density of 3 A/dm² occurs at a low rate. Existence of a kink on the formation dependence (Fig. 1, *a*) indicates the competition of processes of Al_2O_3 formation and dissolution of alloying components the alloy. Under specified conditions in general, prerequisites for cobalt incorporation in the composition of the formed oxide coating are created, however, average concentration of cobalt is low and is a little higher than 2 at. %. Due to low formation rate, quite a lot of silicon (up to 4 at. %) remains on the surface (Fig. 3). For the same reason, a large number of pores remain on the surface in the discharges glow areas (Fig. 2, *a*), although separate areas, consisting of remelts of electrolyte components are formed [31].

An increase in current density of PEO up to 5 A/dm² contributes to intensification of the oxidation process and stabilization of the glow of microarc discharges. The kink on the dependence is not pronounced as much, which indicates faster dissolution of silicon from surface layers and homogenization of their composition. Formation of oxides of aluminum and cobalt with high specific resistance makes it possible to carry out the PEO process for a sufficiently long time interval and to obtain oxide layers, enriched with the doping component. This is proved by the results of the study of morphology (Fig. 2, *b*) and chemical composition of the surface layer (Fig. 3, *b*). Volumetric mosaic structures cover the treated surface and contain up to 5 at.% of cobalt; and silicon concentration is not more than 2 at. %.

PEO at initial current density of 10 A/dm² leads to a rapid formation of a barrier layer of Al_2O_3 by the end of min 1 of treatment. However, the oxidation process is unstable and rather quickly enters the arc mode. Formation voltage after minute 4 of PEO drops to the level of 145–150 V. Large arc discharges, destroying the formed oxide layer, are visualized on the sample's surface. In this case, it is not possible to obtain the coating of the sufficient quality. Morphology of the surface layer (Fig. 2, *b*) is characterized by existence of islet structures with a considerable content of dopant. At the same time, average by the surface cobalt content is negligible and does not exceed 1.5 at. % (Fig. 3, *c*).

Thus, the rational parameters for obtaining coatings with high cobalt content and low concentration of impurities (Si) is to enter the sparking mode within 4–5 minutes and voltage of the micro-arc mode of up to 160–170 V. The optimal combination of the technological parameters of treatment and characteristic properties of the formed coating is achieved at PEO within the range of current densities of 3–5 A/dm² [32].

The dynamics of morphology of surface layers and the content of major components in them can be traced at varying the oxidation time within the specified interval of current densities.

At an increase in treatment time from 10 to 20 minutes, the surface morphology of the samples changes from the structure with islet incorporation of cobalt that is characteristic of barrier aluminum oxide (Fig. 4, *a*), to highly developed mosaic structure (Fig. 4, *b*). This is explained by an increase in thickness of the oxide layer and an increase in content of the dopant, occurring in the sparking mode. Oxidizing within 40 min leads to consolidation of ceramic-like remelts and formation of the structure of voluminous spheroids (Fig. 4, *c*). At a further increase in treatment time up to 60 minutes, the coating surface becomes more uniform (Fig. 4, *d*) due to defects "healing" and inclusion of remelts of electrolyte components, specifically, phosphates [33].

Analysis of the chemical composition of the obtained oxide structures in the areas of different topography indicates enrichment of the surface layer with cobalt at an increase in PEO time. At that, in all cases, its concentration on projections of the coating is 2–3 times higher in comparison with the content on the basic surface. The lowest cobalt content in the coating (up to 0.6 at. %) was obtained at oxidation of samples within 10 minutes (Fig. 5, *a*). The highest concentration of the dopant (up to 23 at. %) is observed in ceramic-like globules of the coating (Fig. 5, *c*) at PEO within 40 minutes. In other cases, cobalt content on the projections is 15–20 at. % and on the plateau of the coating, it is 2–2.5 at. % (Fig. 5, *b, d*). This distribution of the dopant on the surface is explained by peculiarities of the PEO, in which cobalt transport to projections of the sample surface is facilitated, while its transport to pores is complicated. Bearing in mind the possibility of thermolysis of water and release of oxygen on the anode, one may assume that released gases carry the dopant salts out of pores [34].

The inverse dependence is observed for silicon content in surface layers: its concentration decreases at an increase in treatment time. The most effective Si removal from the surface layer is achieved when PEO lasts more than 20 min (Fig. 5, *a–d*), which is explained by chemical instability of silicon oxides in the alkaline medium.

The obtained results are in full accordance with the kinetic patterns and allow us to determine the rational time of PEO for obtaining oxide coatings of the specified composition and morphology.

A high degree of surface development of obtained $\text{Al}_2\text{O}_3\cdot\text{CoO}_x$ coatings is proved by the results of atomic-power microscopy (Fig. 6). The oxide coating, obtained within 10 minutes, consists of a number of conglomerates of spherical structures with an average size of 1.5–2 μm (Fig. 6, *a, c*). An increase in oxidation time up to 20 minutes leads to formation of a voluminous mosaic structure. Taking into consideration the resolution capability of the probe, it is possible to scan effectively its most projected part (Fig. 6, *b*) [35]. The studied ceramic-like structure is a conglomerate and consists of a number of small spherical components, forming a smooth globular surface (Fig. 6, *d*). Indicators of roughness of obtained coatings R_a and R_q are in the range of 0.4–0.5 μm in the studied scan area.

The obtained results indicate that effective PEO-treatment of piston silumin AL25 for obtaining $\text{Al}_2\text{O}_3\cdot\text{CoO}_x$ coatings with a high content of cobalt and developed surface

is implemented at current density of 3–5 A/dm^2 within 20–40 min. Cobalt-containing oxide coatings can be used as catalytically active materials in the air and water purification systems [36].

These technological parameters are applicable for PEO-treatment of aluminum alloys with Si content of 11–13 at. %. A failure to comply with the recommended parameters in the oxidation process and the use of reagents of low quality may be one of the causes of poor-quality treatment of the alloy surface and a decrease in content of catalytically active components of in the composition of oxide coatings.

The prospects of further research are related to adaptation of the proposed technology for surface treatment of other structural materials and expansion of the spectrum of the used dopants. This will make it possible to increase efficiency of the method of surface electrochemical treatment and expand the scope of using mixed oxide systems.

A promising direction of the use of research results is application of the obtained functional materials in intracylinder catalysis of internal combustion engines for reduction of gas emissions toxicity [37].

7. Conclusions

1. The regularities of change in the parameters of plasma-electrolytic oxidation of AL25 alloy in diphosphate cobalt-containing electrolyte were studied. It was found that an increase in current density of the treatment within the interval of 3–10 A/dm^2 leads to a decrease in the time of entering the sparking mode from 6 to 1 min, operating formation voltage is 160–170 V.

2. It was established that a change of the working current density and the time of PEO enables us to control the process of cobalt incorporation in matrix of basic metal oxide. It was shown that an increase in oxidation time up to 20–40 min contributes to enrichment of surface oxide layers with cobalt up to 23.6 at. %. Inclusion of cobalt in composition of surface oxide layers leads to a change of surface morphology and topography.

3. It is advisable to conduct formation of PEO-coatings on AL25 with the developed surface at cobalt content of up to 23 at. % at minimizing silicon content at the level 3 of at. % in the range of current densities of 3–5 A/dm^2 within 20–40 minutes.

References

1. Belov N. A. Fazoviy sostav promyshlennykh i perspektivnykh alyuminievykh splavov: monografiya. Moscow: Izd. dom MISiS, 2010. 511 p.
2. Okada A. Innovative materials for automotive industry. New York: Nova Science Publishers, 2010. 147 p.
3. Obzor tekhnologicheskikh meropriyatiy, napravlennykh na povyshenie nadezhnosti cilindro-porshnevoy gruppy dvigatelya vnutrennego sgoraniya / Nosov A. S., Meleshin V. V., Tovmasyan A. B., Babich A. G. // Sovremennye materialy, tekhnika i tekhnologii. 2017. Issue 3 (11). P. 80–85.
4. Surface Engineering of Light Alloys: Aluminium, Magnesium and Titanium Alloys / H. Dong (Ed.). Elsevier, 2010. 680 p.
5. Electrolytic plasma technology: Science and engineering – An overview / Gupta P., Tenhundfeld G., Daigle E. O., Ryabkov D. // Surface and Coatings Technology. 2007. Vol. 201, Issue 21. P. 8746–8760. doi: 10.1016/j.surfcoat.2006.11.023
6. Ved' M. V. Synthesis and functional properties of mixed titanium and cobalt oxides // Functional materials. 2017. Vol. 24, Issue 4. P. 534–540. doi: 10.15407/fm24.04.534

7. Wear and corrosion resistant coatings on surface of cast A356 aluminum alloy by plasma electrolytic oxidation in moderately concentrated aluminate electrolytes / Xie H., Cheng Y., Li S., Cao J., Cao L. // Transactions of Nonferrous Metals Society of China. 2017. Vol. 27, Issue 2. P. 336–351. doi: 10.1016/s1003-6326(17)60038-4
8. Aluminum- and titanium-supported plasma electrolytic multicomponent coatings with magnetic, catalytic, biocide or bio-compatible properties / Rudnev V. S., Lukiyanchuk I. V., Vasilyeva M. S., Medkov M. A., Adigamova M. V., Sergienko V. I. // Surface and Coatings Technology. 2016. Vol. 307. P. 1219–1235. doi: 10.1016/j.surfcoat.2016.07.060
9. Study into formation of cobalt-containing PEO-coatings on AK12M2MgN from a pyrophosphate electrolyte / Karakurkchi A., Sakhnenko M., Ved M., Horokhivskiy A., Galak A. // Eastern-European Journal of Enterprise Technologies. 2017. Vol. 6, Issue 12 (90). P. 19–27. doi: 10.15587/1729-4061.2017.118028
10. Krishtal M. M. Oxide Layer Formation by Micro-Arc Oxidation on Structurally Modified Al-Si Alloys and Applications for Large-Sized Articles Manufacturing // Advanced Materials Research. 2009. Vol. 59. P. 204–208. doi: 10.4028/www.scientific.net/amr.59.204
11. Xu F., Xia Y., Li G. The mechanism of PEO process on Al-Si alloys with the bulk primary silicon // Applied Surface Science. 2009. Vol. 255, Issue 23. P. 9531–9538. doi: 10.1016/j.apsusc.2009.07.090
12. Production of ceramic coatings on AA6061 aluminium alloy using plasma electrolytic oxidation / Dehnavi V., Luan B. L., Liu X. Y., Shoesmith D. W., Rohani S. // Materials Science and Technology (MS&T 2013) Conference. Montreal, 2013. P. 2247–2254.
13. Ceramic coating formation on high Si containing Al alloy by PEO process / Wang P., Li J. P., Guo Y. C., Yang Z., Wang J. L. // Surface Engineering. 2016. Vol. 32, Issue 6. P. 428–434. doi: 10.1179/1743294415y.0000000003
14. Dudareva N. Y., Abramova M. M. The Structure of Plasma-Electrolytic Coating Formed on Al-Si alloys by the Micro-Arc Oxidation Method // Protection of Metals and Physical Chemistry of Surfaces. 2016. Vol. 52, Issue 1. P. 128–132. doi: 10.1134/s2070205116010093
15. Experimentally Studied Thermal Piston-head State of the Internal-Combustion Engine with a Thermal Layer Formed by Micro-Arc Oxidation Method / Dudareva N., Kal'shchikov R., Dombrovskii O., Butusov I. // Science and Education of the Bauman MSTU. 2015. Issue 5. P. 115–125. doi: 10.7463/0515.0774148
16. Ayday A., Durman M. Growth Characteristics of Plasma Electrolytic Oxidation Coatings on Aluminum Alloys // Acta Physica Polonica A. 2015. Vol. 127, Issue 4. P. 886–887. doi: 10.12693/aphyspola.127.886
17. Rogov A. B., Slonova A. I., Shayapov V. R. Peculiarities of iron-containing microplasma coating deposition on aluminum in homogeneous electrolyte // Applied Surface Science. 2012. Vol. 261. P. 647–652. doi: 10.1016/j.apsusc.2012.08.075
18. Krishtal M. M., Ivashin P. V., Kolomiec P. V. Ispol'zovanie tekhnologii mikrodogovogo oksidirovaniya pri razrabotke DVS s blokom cilindrov iz alyuminiyevogo splava // Izvestiya Samarskogo nauchnogo centra Rossiyskoy akademii nauk. 2012. Vol. 12, Issue 4. P. 242–246.
19. Application of oxide-metallic catalysts on valve metals for ecological catalysis / Karakurkchi A., Sakhnenko M., Ved M., Galak A., Petrukhin S. // Eastern-European Journal of Enterprise Technologies. 2017. Vol. 5, Issue 10 (89). P. 12–18. doi: 10.15587/1729-4061.2017.109885
20. On Composition of Anodic-Spark Coatings Formed on Aluminum Alloys in Electrolytes with Polyphosphate Complexes of Metals / Boguta D. L., Rudnev V. S., Yarovaya T. P., Kaidalova T. A., Gordienko P. S. // Russian Journal of Applied Chemistry. 2002. Vol. 75, Issue 10. P. 1605–1608. doi: 10.1023/a:1022263331315
21. Rudnev V. S. Multiphase anodic layers and prospects of their application // Protection of Metals. 2008. Vol. 44, Issue 3. P. 263–272. doi: 10.1134/s0033173208030089
22. Formation of coatings of mixed aluminum and manganese oxides on the AL25 alloy / Sakhnenko N. D., Ved' M. V., Androshchuk D. S., Korniy S. A. // Surface Engineering and Applied Electrochemistry. 2016. Vol. 52, Issue 2. P. 145–151. doi: 10.3103/s1068375516020113
23. Rogov A. B. Plasma electrolytic oxidation of A1050 aluminium alloy in homogeneous silicate-alkaline electrolytes with edta 4- complexes of Fe, Co, Ni, Cu, La and Ba under alternating polarization conditions // Materials Chemistry and Physics. 2015. Vol. 167. P. 136–144. doi: 10.1016/j.matchemphys.2015.10.020
24. Cobalt-containing layers on titanium / Rudnev V. S., Vasil'eva M. S., Bondarenko M. V., Kuryavyy V. G., Kondrikov N. B. // Inorganic Materials. 2007. Vol. 43, Issue 6. P. 642–644. doi: 10.1134/s0020168507060167
25. Cobalt-containing oxide layers on titanium, their composition, morphology, and catalytic activity in CO oxidation / Vasilyeva M. S., Rudnev V. S., Ustinov A. Y., Korotenko I. A., Modin E. B., Voitenko O. V. // Applied Surface Science. 2010. Vol. 257, Issue 4. P. 1239–1246. doi: 10.1016/j.apsusc.2010.08.031
26. Structures and magnetic properties of iron- and cobalt-containing oxide coatings on an aluminum alloy formed in electrolytes via plasma electrolytic oxidation / Rudnev V. S., Morozova V. P., Lukiyanchuk I. V., Adigamova M. V., Tkachenko I. A., Ustinov A. Y. et. al. // Russian Journal of Physical Chemistry A. 2014. Vol. 88, Issue 5. P. 863–869. doi: 10.1134/s0036024414050264

27. A study of synthesis and properties of manganese-containing oxide coatings on alloy VT1-0 / Sakhnenko N., Ved M., Karakurkchi A., Galak A. // *Eastern-European Journal of Enterprise Technologies*. 2016. Vol. 3, Issue 5 (81). P. 37–43. doi: 10.15587/1729-4061.2016.69390
28. Characterization of plasma electrolytic oxidation coatings formed on Mg–Li alloy in an alkaline polyphosphate electrolyte / Ma C., Lu Y., Sun P., Yuan Y., Jing X., Zhang M. // *Surface and Coatings Technology*. 2011. Vol. 206, Issue 2-3. P. 287–294. doi: 10.1016/j.surfcoat.2011.07.019
29. Sakhnenko N. D., Ved M. V., Karakurkchi A. V. Nanoscale Oxide PEO Coatings Forming from Diphosphate Electrolytes // *Springer Proceedings in Physics*. 2017. P. 507–531. doi: 10.1007/978-3-319-56422-7_38
30. Electrochemical deposition of Fe–Mo–W alloy coatings from citrate electrolyte / Karakurkchi A. V., Ved' M. V., Yermolenko I. Y., Sakhnenko N. D. // *Surface Engineering and Applied Electrochemistry*. 2016. Vol. 52, Issue 1. P. 43–49. doi: 10.3103/s1068375516010087
31. Model concepts on the mechanism of microarc oxidation of metal materials and the control over this process / Rakoch A. G., Khokhlov V. V., Bautin V. A., Lebedeva N. A., Magurova Y. V., Bardin I. V. // *Protection of Metals*. 2006. Vol. 42, Issue 2. P. 158–169. doi: 10.1134/s003317320602010x
32. Mixed alumina and cobalt containing plasma electrolytic oxide coatings / Yar-Mukhamedova G. S., Ved' M. V., Karakurkchi A. V., Sakhnenko N. D. // *IOP Conference Series: Materials Science and Engineering*. 2017. Vol. 213. P. 012020. doi: 10.1088/1757-899x/213/1/012020
33. Role of Phase Composition of PEO Coatings on AA2024 for In-Situ LDH Growth / Serdechnova M., Mohedano M., Bouali A., Höche D., Kuznetsov B., Karpushenkov S. et. al. // *Coatings*. 2017. Vol. 7, Issue 11. P. 190. doi: 10.3390/coatings7110190
34. Examining the formation and properties of TiO₂ oxide coatings with metals of iron triad / Sakhnenko M., Karakurkchi A., Galak A., Menshov S., Matykin O. // *Eastern-European Journal of Enterprise Technologies*. 2017. Vol. 2, Issue 11 (86). P. 4–10. doi: 10.15587/1729-4061.2017.97550
35. Senesi G. S., Massaro A. AFM Applications to the Analysis of Plasma-Treated Surface Growth and Nanocomposite Materials // *Current Nanoscience*. 2016. Vol. 12, Issue 2. P. 202–206. doi: 10.2174/1573413711666150928194029
36. Functional mixed cobalt and aluminum oxide coatings for environmental safety / Ved' M. V., Sakhnenko N. D., Karakurkchi A. V., Myrna T. Yu. // *Functional Materials*. 2017. Vol. 24, Issue 2. P. 303–310. doi: 10.15407/fm24.02.303
37. Increasing the efficiency of intra-cylinder catalysis in diesel engines / Parsadanov I. V., Sakhnenko N. D., Ved' M. V., Rykova I. V., Khyzhniak V. A., Karakurkchi A. V., Gorokhivskiy A. S. // *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2017. Issue 6. P. 75–81.